



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number: **0 460 796 A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **91303527.5**

(51) Int. Cl.⁵: **C23C 14/10**

(22) Date of filing: **19.04.91**

(30) Priority: **20.04.90 US 513354**
20.04.90 US 513302

(43) Date of publication of application:
11.12.91 Bulletin 91/50

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(71) Applicant: **E.I. DU PONT DE NEMOURS AND COMPANY**
1007 Market Street
Wilmington Delaware 19898 (US)

(72) Inventor: **Deak, Gedeon Imre**
14 Ravine Road
Wilmington, Delaware 19810 (US)
Inventor: **Jackson, Scott Christopher**
505 Beechwood Drive
Kennett Square, Pennsylvania 19348 (US)

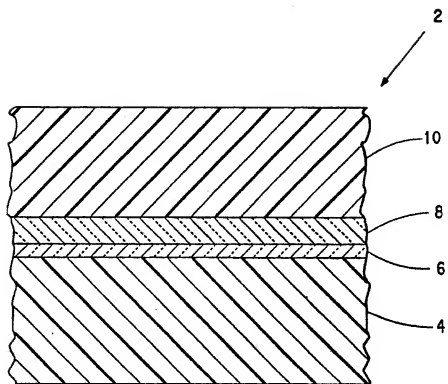
(74) Representative: **Jones, Alan John et al**
CARPMAELS & RANSFORD 43 Bloomsbury Square
London, WC1A 2RA (GB)

(84) Barrier materials useful for packaging.

(57) Improvements to silicon oxide coatings on polymeric substrates are disclosed, which provide improved barrier properties. One improvement involves doping an SiO₂ coating with one or more of certain metals. Another improvement involves first, forming an SiO coating on the substrate, followed by an SiO₂ coating. Another improvement involves the combination of the SiO/SiO₂ coatings plus the incorporation of certain metal dopant into the SiO₂ layer.

EP 0 460 796 A2

Figure 1



FIELD OF THE INVENTION

This invention relates to polymeric films having improved barrier properties towards oxygen and other materials.

Description of Related Art

Flexible polymer films have been used extensively in the packaging of food, electronic and medical products. It is desirable in many applications to have a good barrier to oxygen and/or water vapor. However, most polymer based barrier resins such as ethylene vinyl alcohol copolymer ("EVOH") or polyvinylidene chloride ("PVDC"), although exhibiting good barriers to oxygen or moisture, do so only under ideal conditions. Although EVOH can be an excellent oxygen barrier, it loses its barrier property at moderate to high relative humidity. Thus this material is not widely usable in applications involving high water vapor content, such as moist foods. Although PVDC exhibits good moisture and oxygen barrier properties, it is not suitable for many applications, has an undesirable yellow color, and is difficult if not impossible to recycle. Other proposed alternatives to provide oxygen and water vapor barriers include laminations of aluminum foil and aluminum metallized film. Although these exhibit good barrier properties, they are completely opaque, cannot be recycled, and cannot be readily used for food packaging destined for use in a microwave oven.

U.S. Pat. 3,442,686 discloses multilayer structures as flexible transparent packaging film having good barrier properties to gases and liquids, comprising a flexible transparent organic polymeric base film having thereon an adherent, transparent, flexible highly gas- and liquid-impermeable, moisture resistant, continuous glassy coating of inorganic material, and a sealable, flexible, transparent top coating of organic polymeric material. The glassy coating is sandwiched between the base film and top coating. The preferred base films disclosed include polyester films such as Mylar® oriented, heat set polyester film. The preferred glassy coatings disclosed are the oxides of silicon and aluminum, and the coating thickness is disclosed to be 0.02 to 2 microns (20 to 2000 nm). Among the silicon oxides disclosed are silicon monoxide (SiO) and silicon dioxide (SiO₂). The glassy coating is formed on the base film by vacuum deposition. Examples of sealable top coatings disclosed are polyethylene and vinylidene chloride/acrylonitrile copolymer.

SiO is known to have better barrier properties than SiO₂ but unfortunately SiO is much more expensive than SiO₂ and imparts a yellow color to the package in the coating thickness required for development of its good barrier properties.

Nevertheless, after all the years since publication of U.S. Patent 3,442,686 in 1969, a commercial product has finally been introduced (in Japan) in which the glassy coating is a layer of SiO sandwiched between two layers of polyethylene terephthalate (PET) film and a cast polyolefin top coating to form a packaging film. For one of the products, the SiO layer thickness is on the order of 2000 Angstroms (200 nm). Another product consists of a laminate in which two superimposed layers of SiO are present, each having a thickness of 1200 Angstroms (120 nm), giving a total effective SiO thickness of 2400 Angstroms (240 nm). These products have two disadvantages. First the product has a distinctly yellow color arising from the SiO layer(s) at the layer thicknesses involved, i.e., SiO has a yellow color, which becomes more intense as its thickness increases. It is believed that the yellow color of the SiO coating is somewhat ameliorated by carrying out the vapor deposition of the coating in the presence of oxygen, whereby the SiO is on the order of SiO_{1.5}. Second, the packaging film constituting this commercial product has the disadvantage of high cost arising from the high thickness and high relative cost of SiO present in the packaging film to provide the needed barrier properties. To their credit, however, these packaging films are reported to be able to survive retorting at 125°C without loss of barrier property.

Effort has been made to use SiO₂ coating instead of SiO for economy reasons and in order to obtain a colorless package. To some extent, the barrier properties of SiO₂ can be improved by increased thickness, but there is a limit to this approach because of decreasing flexibility with increasing thickness.

U.S. Patent 4,702,963 discloses packaging film in which an adhesion layer is first vacuum deposited on a flexible polymer substrate, followed by vacuum deposition of a barrier layer, to confer retortability to the packaging film. The adhesion layer can consist of Cr, which is preferred, co-deposited mixtures of Cr and SiO having at least 20% by weight Cr, among others. The barrier layer is preferably silicon monoxide or silicon dioxide. When silicon dioxide is used, it may be mixed with glass modifiers such as oxides of Mg, Ba, and Ca, or with fluoride of alkaline earth metals, e.g., MgF₂. The glass modifiers serve to alter the color appearance of the overall coating. For example, a chromium/SiO composite film is disclosed to produce a coating with a yellowish appearance, while a neutral gray appearance is disclosed to result from the mixture of SiO₂ with glass modifiers. The specific adhesion/barrier layer systems disclosed in the Examples are primarily chromium as the adhesive layer and SiO or SiO₂ as the barrier layer. The lead-alumina silica glass is used as an adhesive layer, as is Ta-Cr alloy, Ta, Mo, and chromium oxides. In some Examples, the SiO₂ layer is mixed with a modifier. In Table 4,

small changes in adhesion layer thickness are disclosed to greatly diminish light transmission. In addition, retortability is determined from a simulated test in which silicon oxide layer adhesion is reported after retorting but not any barrier property of the multilayer structure. The approach taken in this patent has not achieved commercialization.

Japanese patent application 60-244540 discloses a laminate comprising the formation on the surface of a plastic film a transparent thin layer of one or more materials selected from metals, metal oxides, or glass by means of a dry plating method, providing a laminate with good barrier properties. Suitable metals include aluminum, silicon, iron, gold, silver, copper, chromium, nickel, tin, titanium, and magnesium. Suitable oxides may be the oxides of these metals (such as silicon oxide, which can be mixtures of silicon monoxide and silicon dioxide), and glass. A mixed evaporation or multilayer evaporation may be performed.

Japanese patent application 61-47244 discloses a laminate of a plastic film or sheet on the surface of which has been formed a transparent thin layer by dry plating one or more of the materials selected from metals, oxides of the metals, and glass. Suitable metals include aluminum, silicon, titanium, tin, iron, gold, silver, copper, chromium, nickel, magnesium, or the like. The oxides are those of these metals, or glass. These metals and metal oxides may be evaporated in a mixed state to form a layer or evaporated to form a multilayer. The laminate is said to have excellent gas-barrier performance.

U.S. Patent 4,528,234 discloses a transparent laminate comprising a transparent plastic resin film substrate, a thin transparent layer of at least one metal such as aluminum, tin, iron, zinc, or magnesium formed on the substrate by vacuum deposition, and a carboxyl group-containing polyolefin (e.g. ionomer) layer formed on the metal layer by lamination. Optionally an additional layer of silicon oxide or titanium oxide may be present on one or both sides of the plastic film. Oxygen and moisture impermeability are said to be improved.

Japanese patent application 62-158677 discloses a transparent laminate wrapping material where a thin single or mixed metal oxide layer is an intermediate layer in a laminate structure. The laminate is said to have excellent gaseous oxygen and water vapor barrier properties. Silicon oxide and aluminum oxide-silicon oxide mixtures are effective.

Japanese patent application 62-156943 discloses a vapor-deposited layer built-in type multilayered gas-barrier film or sheet having two or more vapor-deposited layers of metals or metal compounds formed at one or more laminate interfaces of a multilayered synthetic resin film or sheet, having good gas barrier characteristics. Suitable metals include aluminum, zinc, copper, platinum, indium, tin, gold, silver, and silicon. A suitable metal compound is silicon oxide.

Chahroudi, "Glassy Barriers from Electron Beam Web Coaters," paper presented at Annual Technical Meeting of Society of Vacuum Coaters, discloses barriers of silicon oxide or SiO_2 . Oxides of Mg, Ca, Ba, B, Al, In, Ge, Sn, Zn, Ti, Zr, Ce, and MgF_2 are disclosed as modifiers or replacements for silica.

Sekamaki, "Vapor Coating with Silicon Dioxide," discloses barrier properties of film with a thin layer of ceramic such as SiO_2 , in particular silicon oxide.

U.S. Patent 3,522,080 discloses a process for hardening the surface of a synthetic material such as a lacquer film, which includes vapor deposition of layers of silicon oxide (SiO_2 , derived from SiO_2) onto the surface. The silicon oxide can contain 1.5 to 5 percent oxide of chromium, zinc, zirconium, or antimony.

U.K. patent application 2 197 881 discloses a heat resistant vessel made of a thermoplastic polyester resin by forming an inorganic coating layer comprising a silicon compound or a metal oxide-containing silicon compound on a surface of the polyester resin. The inorganic coating layer is obtainable from colloidal polysiloxane compounds. The coating material may further contain additives such as an inorganic filler of e.g. titanium oxide, zirconium silicate, nickel, copper oxide, manganese oxide, alumina, etc.

45 SUMMARY OF THE INVENTION

The present invention provides improved barrier layers based on oxides of silicon. In one embodiment, the present invention provides a structure having superior barrier properties, comprising a polymeric substrate and a glassy coating of silicon dioxide doped with at least one metal selected from the group consisting of antimony, aluminum, chromium, cobalt, copper, indium, iron, lead, manganese, tin, titanium, tungsten, zinc, and zirconium, said coating and metal dopant contained therein being present in an amount which provides an oxygen transmission value through the coated film structure of at most about $5 \text{ mL/day-m}^2\text{-atm}$. Preferably the amount of metal dopant is sufficient to provide an oxygen permeation value for the glassy coating of at most about $3000 \times 10^{-6} \text{ mL-mm/day-m}^2\text{-atm}$. The structure may be a film and may comprise one or more layers of a multiple layer structure.

The invention further provides a process for imparting barrier properties to a polymeric substrate, comprising the steps of selecting a polymeric substrate and vacuum depositing onto the substrate a glassy coating prepared from silicon dioxide and at least one metal selected from the group consisting of antimony, aluminum,

chromium, cobalt, copper, indium, iron, lead, manganese, tin, titanium, tungsten, zinc, and zirconium, wherein the amount of said glassy coating and the amount of metal contained therein is suitable to provide an oxygen transmission value through said film structure of at most about 5 mL/day-m²-atm.

In another embodiment of the present invention, a multilayer structure comprises the resin substrate of polyester or polyamide with sequentially vacuum deposited thin and thicker SiO and SiO₂ layers, respectively, thereon. Preferably, the thickness of the SiO layer on the substrate is about 10 to 75 nm (about 100 to 750 Angstroms) and of the SiO₂ layer deposited on the SiO layer is at least about 20 nm (200 Angstroms), with the thicknesses of these layers being selected to provide the barrier properties desired. The SiO layer at these small thicknesses provides virtually no barrier properties and yellow coloration is either barely perceptible or not perceptible at all. For many of the thicknesses of SiO₂ except at the higher thicknesses virtually no significant barrier properties are present. Together, however, these layers provide barrier properties better than the sum of the individual layers.

In still another embodiment of the present invention, the foregoing-described SiO₂ layer of the preceding embodiment incorporates a dopant selected from a wide variety of metallic materials which have the effect of improving the retortability of the multilayer structure as measured by barrier properties, instead of by a simulated retortability test involving only adhesion testing. The dopant improves the pre-retort barrier properties of the SiO₂ layer if no SiO underlayer were present as in the first mentioned embodiment. In the present invention, however, wherein the SiO underlayer is present, the dopant does not appear to appreciably affect pre-retort barrier properties. Instead, the presence of the dopant used in accordance with this embodiment of the present invention tends to stabilize these properties so that they carry over into the retorted multilayer structure.

Another embodiment of the present invention is the process for making a barrier structure from polyester or polyamide polymer as the resin substrate by carrying out the sequential vacuum deposition to form the SiO and SiO₂ combination of layers described above.

The present invention further provides a similar structure and process in which the dopant is lithium borate.

Description of the Drawing

The drawing is directed to the embodiments of the present invention involving the combination of SiO and SiO₂ layers. The drawing is a schematic cross section of a length of multilayer structure 2 of the present invention, comprising a resin substrate 4 having a layer 6 of SiO vacuum deposited thereon, and a layer 8 of SiO₂ vacuum deposited in the SiO layer. Preferably, for this embodiment, a protective outer layer 10 of adherent plastic resin is present in the multilayer structure.

DETAILED DESCRIPTION OF THE INVENTION

The barrier films of the present inventions are polymeric substrates such as films, coated directly or indirectly with specially selected glass coatings. The polymeric substrates include any having suitable physical and thermal properties for the particular packaging application at hand. The minimum requirement is that they have sufficient thermal and physical properties to withstand the conditions of application of the glass coating, described in more detail below, and exhibit sufficient adhesion to the glass coating. Examples of suitable substrates for use when the SiO₂ is coated directly onto the polymeric substrate include those prepared from polyamides, including amorphous and semicrystalline polyamides, polyethers, polyketones, polyester ethers, and polyesters (including polycarbonates), which are preferred. When it is SiO that is directly coated onto the polymeric substrate, the substrate is selected so as to be compatible with the SiO layer so that it can withstand retorting and provide the desired barrier properties. Polymeric substrates of polyester or polyamide provide this compatibility.

Examples of polyester resins include polyethylene naphthalate, polycarbonate, and polyarylate, and most preferably polyethylene terephthalate ("PET"). Examples of semicrystalline polyamides include polycaprolactam (nylon 6) and condensation polymers of dicarboxylic acids and diamines, such as polyhexamethylene adipamide (nylon 6,6) etc. Examples of amorphous polyamides include hexamethylenediamine isophthalamide, hexamethylenediamine isophthalamide/terephthalamide terpolymer, having iso/terephthalic moiety ratios of 100/0 to 60/40, mixtures of 2,2,4- and 2,4,4-trimethylhexamethylenediamine terephthalamide, copolymers of hexamethylene diamine and 2-methylpentamethylenediamine with iso- or terephthalic acids, or mixtures of these acids. Polyamides based on hexamethylenediamine iso/terephthalamide containing high levels of terephthalic acid moiety may also be useful particularly when a second diamine such as 2-methyldiaminopentane is incorporated to produce a processable amorphous polymer. Typically a substrate, especially a film, will have been oriented, optionally followed by heat setting so as to provide dimensional and thermal stability.

It is preferred that the substrate have a high surface smoothness. In particular when the substrate is polyethylene terephthalate it is preferred that the substrate have a smoothness such that the average height of roughness is less than about 50 nanometers, and most preferably less than about 10 nanometers, as measured on a WYKO™ optical profilometer, Model TOPO-3D from WYKO Co., Tuscon, AZ. Most ordinary PET films have a relatively large degree of surface roughness because of the presence of various internal anti-block and slip additives which are necessary to improve handling properties. An oriented PET film without such additives will have a very smooth surface but cannot generally be handled, i.e., wound and rewound, without introducing excessive wrinkling. However, a practical film with preferred smoothness can be prepared by selectively treating only one surface with a selected antiblock agent, leaving the other surface untreated and smooth.

Application of such an agent to at least one surface of a film is described in U.S. patent 3,808,027, the disclosure of which is incorporated herein by reference. A preferred commercially available substrate is Mylar® polyester film, type D, which has a surface roughness of 2-7 nm. It is believed that films with this superior level of smoothness provide better adhesion of the glass coating to the film, leading in certain instances to improved barrier properties and improved stability under rebot conditions. It is preferred that the glassy coating be applied to the smooth side of such film.

Vacuum deposition of SiO or SiO₂ materials to form a coating or layer on a substrate is a conventional process such as by evaporation of the silicon oxide or sputtering. The evaporative process can be performed using thermal processes such as resistance heating, electron beam heating, or induction heating of the silicon oxide source. This causes the source to vaporize and then deposit on the resin substrate positioned in the vacuum chamber. In sputtering, an ion beam or magnetically confined plasma (magnetron) displaces material from the silicon oxide target, causing this displaced material to deposit on the resin substrate or the SiO layer on the resin substrate, as the case may be. Sometimes these processes are referred to as vapor deposition, but the term "vacuum deposition" is used herein to describe these processes, since both the evaporative process and sputtering are carried out in a vacuum. The background pressure of oxygen present in the vacuum chamber may be altered as desired to control the oxygen to silicon ratio in the SiO or SiO₂ deposited layer.

The area of the substrate to be coated is positioned either in a continuous process or batch process in a chamber within which a vacuum is drawn. When the resin substrate is in the form of a film, the film may be made inaccessible to the vacuum deposition on one surface of the film so that only the opposite surface receives the vacuum deposited layers. When the resin substrate is in the form of a container, the entire container can be positioned within the vacuum chamber. The surface of the resin substrate, exterior or interior, facing the source receives the vacuum deposited coatings. The resin substrate can be repositioned and the coating operations repeated to cover additional surface, such as the opposite side, of the substrate. U.S. Patent 4,552,791 discloses a vacuum deposition arrangement for coating containers with SiO or other oxides, disclosing titanium oxide and aluminum oxide. This vacuum deposition arrangement can be used in the practice of the present invention.

The silicon oxide (SiO or SiO₂) source and the dopant source in several embodiments of the present invention are placed in the vacuum chamber and then exposed to the evaporative or sputtering process. The oxide and dopant displaced from the source(s) then form the coating desired on the resin substrate. The thickness of the coating is determined by the residence time of the substrate in the chamber and/or the active area of silicon oxide and dopant sources present in the chamber relative to the area of substrate present in the chamber and the energy applied per unit of target area.

Sufficient vacuum is drawn within the vacuum chamber that the mean free path of the silicon oxide and dopant molecules is sufficient to reach and therefore enable deposition of the glassy layer on the resin substrate. The vacuum used in the experiments described in the Examples herein generally falls within the range of about 1 to 100 microtorr (760 torr = 1 atm). One skilled in the art will know how to select the proper vacuum for a given vacuum deposition process, including its conditions of operation.

SiO₂-Dopant Layer

In this embodiment of the present invention a layer of doped SiO₂ glass can be applied directly to the substrate. The doped SiO₂ glass coating should be thick enough to adequately improve the barrier properties of the substrate, but not so thick as to seriously degrade transparency of the substrate or to result in loss of durability or flexibility of the glass, when the substrate is a film. Typically coatings of about 20 to about 500 nm are suitable, depending on the effectiveness of the particular glass composition. A thickness of about 50 to about 350 nm is preferred, although for some compositions a thickness of about 200 to 400 nm is desirable; for particularly effective compositions, a coating of 50 to 100 nm is quite adequate.

The doped glass coating is based on silicon dioxide. The actual stoichiometry of the glass in this layer may vary from the nominal oxygen-silicon ratio of 2:1 of SiO₂, for example, due to reactions which may occur during

the vacuum deposition process. A source of silicon dioxide and dopant metal (either in different sources or combined in a single source, either as a powder, a metal wire, or vitrified into a silica glass) is placed in the vacuum chamber and vaporized by heating with an electron beam or a resistance or induction heated furnace, or by sputtering or reactive sputtering by an ion beam or a magnetron source, or the like. The silicon dioxide, along with the dopant metal, condenses to form the desired coating.

The dopant can be incorporated into the SiO_2 layer either by evaporating a single source of a physical or fused mixture of the dopant and SiO_2 , or by co-depositing the dopant and the SiO_2 from two or more sources simultaneously. In both cases, the dopant can be in a metallic form or in the form of an oxide, silicide, silicate, halide, or carbonate, and the like. In the case of depositing from a single source, the proportion of the dopant present in the deposited SiO_2 layer may vary from the composition of the source. Such proportion can be determined for a particular source composition and conditions of vacuum deposition and can be adjusted to the proportion desired by adjustment of the source composition. In case of either deposition method, the composition of the coating can be determined by analysis of atomic absorption using inductively coupled plasma (ICP), which is a conventional analysis procedure. This analysis primarily detects the elemental metal in the SiO_2 . Therefore, the weight percents of dopant disclosed herein are based on the elemental metal of the metal dopant. Thus decomposition products, e.g. CO_2 from carbonates, which do not become part of the SiO_2 layer are not included in weight percents of dopant in that layer. The weight percents of dopant disclosed herein refer to the composition of the SiO_2 layer unless otherwise indicated. These same weight percents may, however, be present in the source(s) for vacuum deposition (co-deposition), and as previously described, the resultant composition of the SiO_2 layer for the vacuum deposition conditions used can then be determined, and the source composition can be adjusted in subsequent runs to obtain the final composition desired. More often, the source composition will be adjusted to provide the barrier properties desired for the multilayer structure rather than analyzing the SiO_2 layer for its dopant content.

The silicon dioxide coating of the present invention is "doped," as described above, with a high level of at least one of a select group of metals. The term "doping" is used herein to describe a deposition with silicon dioxide of a relatively high level of metal, typically 0.5 to about 25 weight percent, as measured in the source, or about 0.5 to about 30 weight percent as measured as metal in the glass coating itself.

The oxidation state of the metal as it resides in the coating matrix of silicon dioxide is not necessarily clearly understood or well defined. Thus if an elemental metal is used as the source for the dopant, the deposited metal atoms or particles may interact with the oxygen atoms of the matrix to form a partially or completely oxidized material. Alternatively, if an oxide of the metal is used as the source, it is not necessarily known nor is it necessarily important whether the metal is deposited into the glassy matrix as the oxide or as the elemental metal. It appears that either the elemental metal or an oxide of the metal or certain other metal compounds, regardless of oxidation state can be suitably used as the source of the dopant metal for the present invention. Such possibilities and equivalents thereof are included within the scope of the present invention when terms such as "metal dopant" or the like are used. The selection of an appropriate source for metal dopant will be within the abilities of one skilled in the art and will be determined by such factors as relative cost and ease of handling. In many cases the metal oxide or especially the elemental metal will be preferred.

Suitable metal dopants for the present invention include antimony, aluminum, chromium, cobalt, copper, indium, iron, lead, manganese, tin, titanium, tungsten, zinc, and zirconium. Preferred metals include chromium, manganese, zinc, and most preferably copper and tin. When one or more of these metals are present, the barrier property of the glass coating and of the structure as a whole is greatly improved. Surprisingly it has been found that many other metals do not show this sort of improvement. Among the metals that are not particularly effective at comparable levels are calcium, vanadium, lithium, nickel, molybdenum, gold, germanium, and selenium. Sulfur is similarly not effective. It is surprising that these elements appear in the same regions of the periodic table with the metals that are effective. The chemical phenomenon that distinguishes between these groups of metals is not understood. It is noted that the metals which form a part of the present invention are generally located to the right of Column II of the Periodic Table, that is, to the right of the alkali metals and the alkaline earth metals.

When a metal dopant from the metals of the present invention is used in the layer of silicon dioxide, the improvement in barrier properties can be dramatic. One customary measurement of barrier properties of a film is its oxygen transmission rate ("OTR", ASTM D-3985-81(1989)) expressed as mL oxygen passage/m²-day-atmosphere. A film of ordinary untreated PET, 23 micrometers thick, typically has an OTR of 75-90; that of a 12 micrometer film is typically 150-180. Addition of a 300 nm coating of SiO_2 reduces the OTR somewhat, to about 10-80. Addition of one or more of the metals of the present invention can routinely reduce the OTR to less than 5. In copper, the most preferred case, addition of even 1 percent to the SiO_2 (measured in the source) can reduce the OTR to as low as 0.5, while use of 5-10 percent copper can result in values as low as 0.3. Use of tin, which is also preferred, provides values nearly as low.

The effectiveness of the barrier properties depends not only on the type of metal involved but also, of course, on the thickness of the glass layer. The effect of total glass thickness can be factored out by focusing on the oxygen permeation value ("OPV," $\text{ml} \cdot \text{mm} / \text{m}^2 \cdot \text{day} \cdot \text{atm}$), which provides a measure of the inherent barrier properties of the glass. A coating of SiO_2 alone exhibits an OPV on the order of 0.1 or higher. The coatings of the present invention exhibit OPV of typically 3×10^{-3} or lower, and in the best cases as low as 1×10^{-4} or better.

The OTR or OPV of a particular film or composition is not a simple linear function of dopant concentration. For each metal dopant there appears to be a certain minimum concentration required to achieve a significant improvement, a concentration range, varying somewhat with the metal but generally within about 0.5 to about 30 weight percent (calculated as elemental metal in total glass layer), where the invention is effective, and a region of higher metal concentration within which the effectiveness diminishes or the optical transparency of the film is adversely affected.

SiO/SiO_2 Combination of Layers

In accordance with this embodiment of the present invention, the SiO coating is deposited on the resin substrate first, followed by deposition of the SiO_2 coating onto the SiO layer. In a continuous process, this will be carried out in successive vacuum chambers or in successive vacuum deposition stations in a single vacuum chamber. The same station may be used in a batch process, with the SiO target being replaced by the SiO_2 target.

In the SiO layer, SiO is the essential component. Cr as required in the adhesion layer in U.S. Patent 4,702,963 when SiO is used therein is not required in the present invention. The SiO need not be entirely monoxide, however, since a minor proportion of SiO_2 may be present either by virtue of carrying out the vacuum deposition in the presence of O_2 or by having SiO_2 present as a minor proportion of the SiO target. The SiO_2 diluent in the SiO layer tends to eliminate any perceptible yellow color from the greater thicknesses within the 10 to 75 nm layer thickness range employed in the present invention. As thickness of the SiO layer increases within this range, both the tendency towards yellow coloration and cost increase, which can be essentially offset by incorporating a minor proportion of SiO_2 in the SiO layer or by other means increasing the atomic ratio of oxygen to silicon. Preferably, the ratio of oxygen to silicon in the SiO layer does not exceed about 1.4 and more preferably, does not exceed 1.25. The ratio of oxygen to silicon can also be less than 1:1, e.g., as low as 0.6 to 1, as can be obtained by using silicon as the source and reacting it with oxygen during the vacuum deposition process. Thus the new SiO layer can have oxygen/silicon ratios in the range of 0.6 to 1.40:1. Excessive amounts of SiO_2 or greater proportions of oxygen in the SiO layer tend to detract from barrier properties of the combined layers. It is important for this embodiment that some thickness of SiO layer be present, since the combination of resin substrate and the SiO and SiO_2 layers provides desirable barrier properties. The preferred SiO layer thickness is about 10 to 50 nm.

The SiO_2 layer in this embodiment will generally not require a thickness of greater than about 500 nm (5000 Angstroms) and preferably has a thickness of about 50 to 350 nm (500 to 3500 Angstroms). The stoichiometry of the SiO_2 layer may vary from the oxygen/silicon ratio of 2:1 such as by reactions which may occur during the vacuum deposition process.

The SiO_2 layer also preferably is "doped" with an effective amount of metallic material which improves the barrier properties of the layer during retorting as compared to barrier properties without dopant being present, and preferably substantially stabilizes the barrier properties so that they do not appreciably deteriorate upon retorting. For demanding barrier utilities, the doped SiO_2 layer in combination with the SiO layer provides results equivalent to SiO at similar overall thickness but without the high cost of SiO . It has been discovered that Ti, Zr, Zn, Al, In, Pb, W, Cu, Sn, Cr, Fe, Mn, Sb, Co, Ba and Mg or oxides, halides, such as chlorides and fluorides, and carbonates, thereof or mixtures thereof vacuum deposited with the vacuum deposition of the SiO_2 layer improves the barrier properties of the layer. Generally the effective amount of metal dopant which improves the barrier properties of the SiO_2 layer will be within the range of about 0.5 to 30% based on the total weight of the layer, and preferably 2 to 15% based on the weight of the layer depending on the particular dopant used and the barrier result desired.

The dopant can be incorporated into the SiO_2 layer in the same manner as described hereinbefore.

The source composition will be adjusted to provide the barrier properties desired for the multilayer structure rather than to analyze the SiO_2 layer for its dopant content.

Despite the presence of dopant in the SiO_2 layer, multilayer structures of the present invention using this embodiment, such structures can be used in microwave food packaging without any appreciable blocking of microwave energy from reaching the food during microwave cooking.

Contrary to the light transmission results reported in U.S. Pat. 4,702,963, the light transmission of multilayer

structures of the present invention are high, preferably not appreciably degrading the light transmission of the resin substrate. The SiO₂ layer, even containing metallic material dopant can be and is preferably colorless, so that the entire multilayer structure is colorless.

As previously stated herein, the metal dopant appears to have the effect of enabling the barrier properties of the multilayer structure to survive retorting, e.g. prolonged contact with boiling water under pressure at temperatures at least 125°C.

One measure of improved barrier properties is reduced oxygen transmission through the multilayer structure.

Multilayer structures of this embodiment of the present invention can achieve barrier properties characterized by an oxygen transmission rate (OTR) of less than about 7 ml/m² Day Atm, preferably before and after retorting. The preferred oxygen transmission rate before and after retorting is less than about 3 ml/m² Day Atm. The oxygen transmission is measured on a Model "OX-TRAN 1000" made by Modern Controls Inc., of Minneapolis MN in accordance with ASTM test D 3985-81 (1988) except that the test is carried out at 30°C and at 80% relative humidity, using 100% (1 Atm pressure) oxygen, with the result being normalized to 1 m² of multilayer structure and one day's duration for the test. The retorting procedure used for these tests involves placing the multilayer structure in a bath of water in an autoclave under 2.5 Atm absolute pressure at 125°C for 30 minutes in addition to the time for heating up (30 minutes) and cooling down (15 minutes) the water bath in which the multilayer structure is immersed.

The other barrier property of primary interest in food packaging is the barrier to water vapor. Multilayer structures of this embodiment of the present invention also exhibit low permeability to passage of water vapor, both before and after retorting. Preferably, the water vapor transmission of multilayer structures of the present invention is no greater than about 5 g/m² from 90% relative humidity to 50% relative humidity, and more preferably no greater than about 3 g/m² (same relative humidity conditions) as measured by ASTM-F 1249.

In all embodiments of the present invention, an additional protective layer for the SiO₂ layer can be added (with or without dopant). Such a layer can be selected from any plastic resin that adheres to the SiO₂ layer or that adheres via an intervening adhesive layer. Examples of protective layers include a layer of polyester (adhered to the SiO₂ layer via an adhesive), polyamides, acrylonitrile copolymers, polyvinylidene chloride, polyethylene, polypropylene, ethylene vinyl acetate copolymer, ethylene/acrylic or methacrylic acid copolymer and ionomer. The protective layer can be applied to the SiO₂ layer by conventional processes such as adhesive or thermal laminating or extrusion coating simultaneous with extrusion of the intervening adhesive, if any. The protective layer can also be provided by solvent or dispersion coating onto the SiO₂ layer, using multiple coatings if thickness greater than achievable by single coating is desired. The thickness of the protective layer will generally be about 0.5 to 100 micrometers, preferably 10 to 25 micrometers (0.010 to 0.025 mm). In one embodiment, the protective layer is biaxially oriented PET film (0.0234 mm thick), which is laminated to the exposed surface of the SiO₂ layer via a co-polyester adhesive resin available as Adcote 506-40 (2.7 g/m²) from Morton Chemicals and a nip roll heated at 120°C for pressing the film and laminate structure against one another.

Films and structures of the present invention are useful as a wide variety of packaging, from rigid to semi-rigid containers to packaging film where barrier properties towards oxygen and other materials are desired. The particular use will dictate the choice and shape of the resin substrate. For packaging films, the resin substrate will be in the form of a film having, for example, a thickness of 10 to 150 micrometers, often 12 to 50 or preferably 15 to 25 micrometers. The high light transmission and colorless appearance of packaging of multilayer structures, especially those which contain the SiO/SiO₂ combination of layers serves as a good showcase for food packaged therein, and the high barrier properties of such packaging provides excellent preservation of this food.

Examples of the present invention are as follows (parts and percents are by weight unless otherwise indicated):

Examples 1-136

Silicon dioxide was mixed with a dopant material and loaded into the hearth (crucible) of an electron beam evaporator of the single crucible bent beam source type as sold by a variety of manufacturers including Denton Vacuum of Cherry Hill, NJ. A thin film was formed from this mixture onto the smoother surface of a 23 micrometer (92 gauge) PET film (Mylar® type D) by electron beam evaporation from the mixture. The accelerator voltage was continuously adjusted to sweep the beam across the material in the source crucible to give uniform erosion of the crucible's contents. The filament current (and hence the beam current) was adjusted to provide a high deposition rate, resulting in a relatively high background pressure of about 1.3×10^{-2} Pa (about 1×10^{-4} torr). This pressure was not so high as to cause premature arc-over of the electron beam gun. The thickness of the deposit was monitored by a calibrated oscillating quartz crystal monitor such as manufactured by Veeco Instruments Inc., Plainview, NY. The film (unless another grade is reported) had an average (RA) surface roughness

of 2-7 nanometers. The coated film's oxygen transmission rate was measured using an "Ox-Tran 1000"TM oxygen permeation device manufactured by Modern Control Inc. of Minneapolis, Minn. All data in Table I were obtained at 30°C at 80% relative humidity, using 100% oxygen at 1 atmosphere pressure (about 101 kPa). The results are reported in the Tables as oxygen transmission rate (mL/m²-day-atm). In addition the results are reported as oxygen permeation value (mL-mm/m²-day-atm) by subtracting the (minimal) barrier properties of the uncoated film and dividing the result by the thickness of the glass coating.

The results for the first Examples, Table 1, Examples 1-11, illustrate the poor barrier properties of PET film treated with a layer of undoped silicon dioxide.

TABLE I

<u>Ex.a</u>	<u>Dopant</u>	<u>Thickness, nm</u>	<u>OTR</u>	<u>OPV X 10⁶</u>
C1	none	325	23.6	12054
C2	"	300	84.3	>100000
C3	"	301	76.4	>100000
C4	"	303	77.1	>100000
C5	"	314	7.1	2517
C6	"	315	62.1	>100000
C7	"	323	51.6	83026
C8	"	355	10.1	4238
C9 ^b	"	--	161.5	--
C10 ^b	"	--	72.4	--
C11 ^b	"	--	28.1	--

- a. Examples designated "C" are included for comparative purposes.
- b. PET film having a surface roughness of 26-33 nm and a thickness of 12 micrometers.
- indicates value not measured.

The results in the next series of Examples, Table II, Examples 12-57, illustrate many of the metal dopants which are not a part of the present invention. Most of these dopants do not provide significant improvements in barrier properties in the concentration ranges examined, although a few do show improvement (e.g. MgF₂, MgO, BaO, disclosed in U.S. 4,702,963 along with CaO which does not show adequate activity). For reasons which are not fully understood, low levels of lithium borate, Li₂B₄O₇, seem to be effective and are thus considered to be included within the scope of the present invention.

TABLE II

Ex.	Dopant, %	Thickness, nm	OTR	OPV X 10 ⁶
5	C12 Ag 10	301	8.5	2944
	C13 AgO 10	300	5.9	1944
	C14 BaO 10	307	2.6	828
	C15 " 30	315	7.7	2743
10	C16 B ₂ O ₃ 3	326	80.3	>100000
	C17 " 10	213	77.2	>100000
	C18 " 10	327	83.4	>100000
15	C19 Ca(BO ₂) ₂ 10	290	74.7	>100000
	C20 " 10	303	35.5	23832
	C21 " 25	239	82.5	>100000
	C22 " 50	230	73.2	>100000
20	C23 CaO 10	301	6.0	1985
	C24 " 30	265	12.3	4042
	C25 K ₂ O 10	308	27.0	14319
25	C26 Li 3	--	80.6	--
	27 Li ₂ B ₄ O ₇ 1	307	2.5	797
	28 " 2	301	2.4	756
	C29 " 7	301	41.5	34897
	C30 LiF 1	301	30.1	17002
	C31 " 4	300	50.4	68597
30	C32 MgCl ₂ 2	301	51.7	78306
	C33 " 10	246	19.0	6639
	C34 " 10	246	23.3	8955
35	C35 MgF ₂ 1	303	20.6	9185
	C36 " 2	299	1.1	320
	C37 " 5	105	4.0	449
	C38 " 5	201	2.2	455
	C39 " 5	303	1.1	334
40	C40 " 10	297	1.1	328
	C41 " 10	308	1.1	340
	C42 " 15	306	2.2	713
	C43 " 30	--	10.2	--
45	C44 MgO 5	304	1.9	602
	C45 " 10	302	5.4	1766
	C46 " 35	215	1.6	341
	C47 " 35	306	1.6	486
50	C48 Na ₂ B ₄ O ₇ 4	321	29.9	17889
	C49 " 10	--	57.2	--
	C50 " 10	265	66.0	>100000
	C51 Na ₂ SO ₄ 5	302	60.2	>100000
	C52 " 20	304	70.3	>100000

Table II, continued				
C53	Na+Al ^a		301	73.1 >100000
C54	Mo	10	302	72.7 >100000
C55	Ni	10	299	55.8 >100000
C56	Si	10	304	3.3 1073
C57	"	20	307	1.5 463

a. A fused glass; exact composition unknown.

The next series of Examples, Table III, Examples 58-67, show certain metal compound dopants (AlF₃, CuCO₃, CuF₂, Cu₅Si, and WO₂) which are effective only at comparatively higher concentrations in the source, e.g., about 20%. It is believed that these materials evaporate at a slower rate than does SiO₂, resulting in lower actual concentrations in the films. Yet it is believed that when a sufficient amount of metal is deposited in the glass coating, the results nevertheless show significant improvement in barrier properties.

TABLE III

Ex.	Dopant, %	Thickness, nm	OTR	OPV X 10 ⁶
C58	AlF ₃	2 302	19.5	8445
59	"	10 313	2.9	961
C60	CuCO ₃ -			
	Cu(OH) ₂	5 302	15.3	6038
61	CuCO ₃	20 300	1.6	491
62	CuF ₂	5 273	9.8	3152
63	Cu ₅ Si	5 308	78.9	>100000
64	"	20 302	1.9	588
65	"	20 302	0.9	275
C66	WO ₂	5 286	79.9	>100000
67	WO ₃	20 123	4.1	537

The last series of Examples, in Table IV, Examples 68-136, illustrate the results using metal dopants of the present invention. Concentrations of metal within the effective concentration ranges provide marked improvements in barrier properties. (In some of the examples using copper, the metal was added to the source material in the form of a wire; in other examples, as a powder. No consistent differences in the results were observed.)

TABLE IV

	Ex.	Dopant, %	Thickness, nm	OTR	OPV X 10 ⁶
5	68	Al	2 303	1.9	595
	69	"	10 303	1.3	403
	70	"	10 311	1.6	494
	71	"	15 312	4.5	1496
10	C72a	"	30 321	14.3	5875
	73	Co	10 214	0.9	196
	74	Cr	10 303	1.3	408
15	75	"	20 302	1.9	603
	76	"	30 300	0.7	207
	77	"	30 302	1.3	387
	C78	Cu	1 300	8.1	2793
	C79a	"	1 300	124.0	>100000
20	80	"	1 301	0.5	160
	81	"	2 26	3.7	102
	82	"	2 52	4.9	276
	83	"	2 301	0.7	198
	84	"	3 303	4.1	1334
25	85b	"	5 --	0.7	---
	C86	"	5 28	11.4	388
	87	"	5 51	2.1	109
	88	"	5 100	0.9	90
	89	"	5 301	0.5	160
30	90	"	5 301	1.0	308
	91	"	5 303	0.3	80
	92c	"	5 305	2.6	829
	93d	"	5 300	2.5	770
	94e	"	5 295	2.2	658
35	C95f	"	5 300	7.6	2428
	96g	"	5 298	5.1	1712
	97h	"	5 300	0.9	271
	98h	"	5 302	1.8	567
	99i	"	5 301	1.5	527
40	100	"	5 301	0.9	289
	C101	"	5 303	60.3	>100000
	C102	"	10 26	7.6	225
	103	"	10 28	2.9	84
45	104	"	10 51	2.9	155
	105	"	10 102	3.3	360
	106	"	10 117	2.1	257
	107	"	10 301	0.3	94
	108	"	10 301	0.5	155
	109	"	15 100	1.3	136
50	110	"	20 301	2.3	726
	111	"	30 300	0.6	188

55

Table IV, continued

	C112	Cu, B ^k	5	302	74.1	>100000
	113	Cu(NO ₃) ₂	5	253	3.5	933
5	114	Fe	5	302	1.4	421
	115	"	10	304	3.6	1174
	116	In	5	302	1.6	509
10	117	"	20	309	1.5	476
	118	Mn	10	302	0.6	189
	119	Pb	10	330	1.5	497
	120	"	20	309	1.7	526
15	121	Sb	5	190	5.8	1093
	122	Sn	5	302	1.2	358
	123	"	5	304	1.1	335
20	124	"	5	130	1.6	256 (est.)
	125	"	10	150	3.3	524
	126	"	20	303	1.0	296
	127	"	30	54	6.2	373
	C128 ^a	"	30	54	146.8	>100000
25	C129	316 stainless steel ¹	10	305	5.3	1767
	130	TiO ₂	10	300	3.8	1200
30	131	Zn	10	65	6.2	448
	132	"	10	257	1.4	375
	133	"	10	296	5.9	1913
	134	"	20	304	2.2	688
35	135	ZnO	10	308	1.8	555
	136	{ Zn 5 } { Cu 2 }	301		3.9	1262

- 40 a. Borderline example; results subject to scatter.
 b. PET film "Melinex Type 442," surface roughness 10-18 nm. Coating thickness not measured.
 c. PET film having a surface roughness of 10-18 nm and a thickness of 14 micrometers.
 d. PET film having a surface roughness of 26-33 nm and a thickness of 12 micrometers.
 e. PET film having a surface roughness of greater than 26 nm and a thickness of 23 micrometers.
 45 f. Polyester film having a surface roughness of 41-49 nm and a thickness of 12 micrometers.
 g. Laminate of the coated film to a layer of uncoated 12 micrometer PET, using copolyester adhesive sheet.
 h. Laminate of the coated film to a layer of PET having a coating of heat sealable polyester copolymer, using copolyester adhesive sheet.
 i. Laminate of the coated film to a layer of PET coated with PVDC, using copolyester adhesive sheet.
 50 j. Substrate film poly(ethylene-2,6-naphthalene dicarboxylate) with 30 nm undercoating of SiO.
 k. Fused silica glass containing Cu and B.
 l. 18% Cr, 11% Ni, 2.5% Mo, <0.1% C, remainder Fe.

Examples 137-175

55

In the previous Tables the amount of dopant is listed as the amount present in the source in the hearth of the evaporator. The actual amount present in the glass coating was independently measured for some samples by atomic absorption. About 2-2.5 g of the sample is weighed accurately and charred with concentrated sulfuric

acid, then dissolved by addition of concentrated nitric acid (aqua regia) and concentrated hydrofluoric acid and heating. The solution is diluted to 100 mL and analyzed by an Applied Research Laboratories 34000 simultaneous inductively coupled plasma analyzer or a Perkin Elmer 6500 (sequential) inductively coupled plasma analyzer. The amounts of the reported elements are calculated assuming that the dopant is the elemental metal and the matrix is SiO_2 (m.w. 60). The results are shown in Table V.

		Table V		
		Thickness		
	Ex.	Dopant	(nm)	Source % Coating %
10	C137	Ag	303	10.0 0.1
	C138	B_2O_3	300	10.0 0.7
	C139	MgF_2	302	5.0 0.6
	C140	"	301	10.0 1.0
15	C141	Mo	301	10.0 13.4
	C142	$\text{Na}_2\text{B}_7\text{O}_{14}$	302	10.0 {2.1 Na}
				{1.3 B }
	C143	Ni	300	10.0 16.3
20	144	Al	302	5.0 3.8
	145	"	312	10.0 4.0
	146	"	303	10.0 <1.8
	147	Fe	298	5.0 7.4
25	148	"	304	10.0 13.5
	149	Cr	301	2.0 3.2
	150	"	301	5.0 8.8
	151	"	298	5.0 7.7
30	152	"	304	10.0 14.6
	153	"	301	10.0 14.1
	154	Cu	147	5.0 10.5
	155	"	299	5.0 0.0
35	156	"	300	5.0 1.5
	157	"	307	5.0 8.7
	158	"	310	5.0 7.4
	159	"	152	10.0 15.8
	160	"	299	10.0 8.7
40	161	"	303	10.0 6.2
	162	"	305	10.0 21.2
	163	"	276	10.0 17.1
	164	"	301	20.0 30.2
	165	"	153	20.0 29.8
45	166	Mn	302	10.0 12.9
	167	Sn	301	2.0 8.8
	168	"	152	5.0 12.2
50	169	"	304	5.0 24.3
	170	"	302	5.0 17.5
	171	"	301	5.0 12.0
	172	"	271	5.0 8.8
	173	"	153	10.0 14.6
55	174	"	306	10.0 24.7
	175	"	285	10.0 26.4

The considerable scatter in the analysis of the coating composition is believed to arise from several sources

Including inaccuracies in the atomic absorption technique and the use of a laboratory evaporation method which uses a powder mixture of the components which may be less reproducible than desired. However correlations can be obtained which indicate actual coating compositions with a calculable uncertainty. The results relating to the metals included in the present invention all indicate a higher concentration of the dopant metal in the coatings than in the source, with the possible exception of aluminum and silver. These trends are believed to be related to the relative vapor pressures of the metals compared with silicon dioxide. In particular the amount of copper or chromium in the glassy coating is about 1.4-1.5 times the amount in the source; the amount of tin in the coating is about 2.4-2.5 times the amount in the source. Metal compound dopants, for example some metal oxides, which may have lower vapor pressures than the elemental metals, may exhibit different correlations from those seen for the elemental metals. This phenomenon would explain the behavior of the examples in Table III, which require higher concentrations in the source to be effective. However, differences in vapor pressure cannot explain the ineffectiveness of such metals as nickel or molybdenum, which do appear in the coatings in amounts comparable to those for e.g. copper.

Examples 176-209

The Examples in Table VI show the effect of increasing dopant levels on visible light transmission of films prepared according to the procedure of Examples 1-136 using a batch "bell-jar" process. The visible light absorbance (from which transmission is calculated) was measured using a Hewlett-Packard 8452A diode-array UV-vis spectrophotometer, having a bandwidth of 2 nm, wavelength reproducibility of ± 0.05 nm, and stability of < 0.002 absorbance units. The device measures the entire UV and visible absorbance spectrum simultaneously without scanning. The zero absorbance level was defined using air as the blank. For each film the absorbance spectrum from 360 to 740 nm was measured and stored on disk. The absorbances at 400 and 550 nm are reported. It is observed that percent transmission decreases with increasing dopant level; preferred films are those which retain at least about 70 percent transmission at 550 nm. Iron, chromium, and tin appear to be preferred in minimizing loss of optical transmission. Iron appears particularly suitable in this regard and actually appears to enhance the optical transmission.

Table VI

Ex.	Dopant, %	Thickness (nm)	% Transmission	
			400 nm	550 nm
C176	(no coating)		85.01	88.71
C177 ^a	(no coating)		69.25	77.34
C178	none	--	323	81.85 83.18
C179	"		303	75.68 83.56
C180	MgF ₂	5	201	88.10 88.10
181	"	5	306	88.98 90.19
182	"	10	301	86.90 92.17
C183 ^b	SF ₆	5	306	86.60 87.70
184	Al	5	304	76.21 80.91
185	"	15	312	38.90 75.86
186	"	30	321	1.45 28.18
187	Cr	5	304	84.96 88.73
188	"	10	152	82.45 82.42
189	"	10	303	85.62 90.07
190	"	20	76	81.16 83.67
191	"	20	153	70.89 78.76
192	"	20	302	12.30 31.62
193	Cu	5	300	59.57 71.94
194	"	5	301	73.79 81.66
195	"	10	117	64.12 72.44
196	"	10	311	51.71 71.94
197	"	20	78	84.96 88.73
198	"	20	155	50.05 61.44
199	"	20	301	25.59 39.81
200	"	20	302	53.48 65.80
201	Fe	5	302	87.90 89.41
202	"	10	304	82.99 89.54
203	Mn	10	302	78.16 83.95
204	Pb	10	330	26.61 41.88
205	Sn	5	302	85.11 88.72
206	"	10	150	82.70 85.51
207	"	10	311	84.45 85.29
208	"	20	76	86.50 90.16
209	"	20	303	25.94 36.31

a. Commodity PET film with internal slip additive, 24 micrometers thick.

b. Coating prepared from lead glass - about 70% Pb.

Example 210

This Example demonstrates the improvement provided by the SiO/SiO₂ multilayer combination in terms of barrier properties.

Layers of the silicon oxides were formed by electron beam evaporation on the side of Mylar® D PET film (0.0234 mm thick) without slip nodules to form a barrier film.

Details of the electron beam evaporation procedure are as follows: the electron beam evaporator used was the type using a single crucible bent beam source. There are several different manufacturers of equipment providing this beam source, e.g., Leybold AG, Alzenau, West Germany; Balzers AG, Furstentum Liechtenstein; Temescal of Berkeley, CA.; or Denton Vacuum of Cherry Hill, New Jersey, the latter being used in this Example.

The accelerator voltage was continuously adjusted to sweep the electron beam across the material in the crucible forming the hearth of the electron beam evaporator to give a uniform erosion of the crucible's silicon oxide contents. The filament current (and subsequently the beam current) was adjusted to give a high deposition rate which resulted in a relatively high background pressure of about 1×10^{-4} torr. This pressure was not so high as to cause premature arc over of the electron beam gun. The thickness of the deposits were monitored by a calibrated oscillating quartz crystal monitor such as made by Veeco Instruments Inc., Plainview, New York, and the vacuum deposition process was stopped when the desired oxide layer thickness was reached.

The results of the experiments reported under this Example are shown in Table VII.

Table VII - Barrier Film O₂ Permeability

SiO layer thickness (nm) <u>on the PET film</u>	SiO ₂ layer thickness (nm) on the SiO <u>layer</u>	OTR (no retort) (ml/m ² Day Atm)
31	0	43.2
0	355	10.1
0	301	76.4
0	303	77.1
0	314	7.1
0	300	84.3
0	315	62.1
30	202	1.1
102	184	2.3
35	237	1.2
15	214	2.5

OTR is the ml of O₂ transmitted across the multilayer structure in one day with a partial pressure difference of one atmosphere of oxygen, under the further conditions described hereinbefore. In this Example, the OTR was determined on unretorted barrier film.

Experiments h., j., and k. are examples of the present invention and provide the lowest oxygen permeability, demonstrating the best barrier properties when the combination of SiO and SiO₂ layers are used.

Experiment a. shows that the thin layer of SiO by itself on the PET film substrate provides poor barrier property. The film by itself exhibits an oxygen permeability of 75 ml/m² Day Atm.

Experiments b. through g. show that the thicker SiO₂ layers used by themselves (no SiO underlayer) provide variable oxygen permeability results as compared to Experiment a., i.e., sometimes better, sometimes worse.

The combination of SiO and SiO₂ layers, however, as shown in experiments h., j., and k. provides better barrier properties than demonstrated by either the SiO or SiO₂ layers used separately, with a more than 200% improvement over the best results exhibited by the SiO₂ layers used by themselves (on PET film).

Experiment i. demonstrates that thicker SiO and thinner SiO₂ layers may be used in the combination but at sacrifice in economy because of the greater cost of SiO as compared to SiO₂ and color. The multilayer film structures of experiments h., j., and k. are transparent and colorless as are the film structures of experiments a. through g., while the film structure of experiment i. exhibits yellow coloration.

Example 211

A multilayer film structure of a layer of 31 nm thickness of SiO on the PET film used in Example 210 and a layer of 202 nm thickness of SiO₂ on the SiO layer was prepared in the same manner as Example 210 and the resultant colorless barrier film was subjected to retorting by placement in a bath of water in an autoclave at 125°C for 30 minutes. While the film was unchanged in visual appearance to the naked eye, the OTR of the film degraded to 39.8 ml/m² day Atm, suggesting that this combination should be used where the film structure would not be subjected to retorting, e.g., for packaging tea, coffee, cereals, and cigars.

Example 212

This example shows the effect of varying the stoichiometric ratio of oxygen to silicon in the SiO underlayer formed on the PET film. The multilayer structure: PET film/SiO/SiO₂, by the procedure of Example 210, using the PET film used in that Example, with the following results:

Table VIII

	SiO	SiO ₂	OTR
	Layer thick-	Layer thick-	(after retort)
Ratio of O:Si	ness (nm)	ness (nm)	(ml/m ² Day Atm)
1.25:1	54	283	0.9
1.5:1	31	240	>150

In the experiments addressed in Table VIII, the SiO₂ layer was doped with Sn by vacuum deposition by electron beam evaporation of a 95/5 weight source mixture of SiO₂ and Sn. The SiO layer was formed to contain the greater proportion of oxygen as indicated in Table VIII by mixing SiO and SiO₂ together in the weight ratio indicated to form a single source (target). The permeability testing was carried out after retorting of the film structure by the procedure described in Example 211. From these results it can be seen that as the oxygen ratio increases in the SiO underlayer, the retortability of the multilayer structure decreases.

Example 213

This Example shows the effect of SiO layer thickness on barrier properties for PET film/SiO/SiO₂ multilayer film structure by the procedure of Example 210, using the PET film used in that Example, with the following results:

Table IX

SiO layer	SiO ₂ layer	OTR (after retort)
thickness nm	thickness	(ml/m ² Day Atm)
2	238	81.0
5	241	84.9

The SiO₂ layer in this Example was doped with 5% Sn in the same manner as reported for Table VIII and the oxygen permeability was determined after the film structure had been retorted as described in Example 211. This retorting virtually destroyed the barrier property of the film structure whereas for the thicker SiO layer used in the first experiment of Table VIII, excellent barrier property was exhibited after retorting even though the SiO layer was somewhat diluted by its 1.25:1 O₂ to Si ratio.

Example 214

In this example, the film structure PET film/ 13 nm SiO/308 nm SiO₂+5% Cu (source mixture) was prepared and tested for oxygen permeability by the same procedure as Example 210, but after retorting by the procedure of Example 211, and the resultant OTR was 2.8 ml/m² day Atm indicating that a moderately thin SiO layer serves

to provide reasonably good barrier property in combination with the SiO_2 layer.

Example 215

5 A 49 nm thick layer of SiO was formed onto a 92 gauge (0.0234 mm) "Mylar D" PET film by electron beam evaporation in a vacuum chamber as described in Example 210. The deposit was transparent and exhibited a yellow color which was barely perceptible. A second layer, 250 nm thick of SiO_2 mixed with 5% MgF_2 dopant (Mg weight basis) as the source in the hearth of the electron beam evaporator, was formed on top of the SiO layer by electron beam evaporation. The resultant barrier film was transparent, clear and colorless. This coated film was then retorted by placing it into a bath of water in an autoclave at 125°C for 30 minutes. The retorted film's oxygen transmission rate (OTR) was 1.04 ml/m^2 day Atm, and the film retained the transparent, clear, and colorless appearance present in the unretorted film.

For comparison purposes, SiO_2 was mixed with 5% MgF_2 (Mg weight basis). This mixture was loaded in the hearth as the source of an electron beam evaporator. A film of approximately 301 nm was formed directly onto a 92 gauge "Mylar D" PET film (on the side without the slip nodule additive) by electron beam evaporation from this mixture. The deposit was transparent and clear. This coated film was then retorted by placing it into a bath of water in an autoclave at 125°C for 30 minutes. The retorted film's oxygen transmission rate (OTR) was measured as 94 ml/m^2 day Atm which was even greater than the barrier quality of the of "MYLAR" base film without the SiO_2 layer. Furthermore, instead of being a clear film, the SiO_2 layer while still transparent, exhibited a great amount of crazing or many small cracks. Repetition of the experiment to obtain a SiO_2 layer 301 nm thick but without the MgF_2 dopant gave similarly poor barrier property, except that the SiO_2 layer had good adhesion to the PET film as indicated by high peel strength (152 g/cm), and was transparent and colorless, without any cracks or crazing being visible to the naked eye.

25 Example 216

A 50 nm film of SiO was deposited onto a 92 gauge "Mylar D" PET film (on the side without the slip additive) by electron beam evaporation. The deposit was transparent. A second layer, 252 nm of SiO_2 mixed with 5% Sn dopant (in the hearth of the electron beam evaporator), was deposited on top of the SiO layer by electron beam evaporation. The film remained transparent and clear after this second deposit. This coated film was then retorted by placing it into a bath of water in an autoclave at 125°C for 30 minutes. The retorted film's oxygen transmission rate (OTR) was measured as 0.65 ml/m^2 Day Atm and the film retained its transparency and clarity.

For comparison purposes, SiO_2 was mixed with 5% of Sn. This mixture was loaded in the hearth of an electron beam evaporator. A film of approximately 298 nm was formed onto a 92-gauge "Mylar D" PET film (on the side without the slip additive) by electron beam evaporation from this mixture. The deposit was transparent and clear. This coated film was then retorted by placing it into a bath of water in an autoclave at 125°C for 30 minutes. The retorted film's oxygen transmission rate (OTR) was measured as 97 ml/m^2 Day Atm, which was greater than the barrier property of the base film by itself. Furthermore, instead of being a clear film, the glass deposit exhibited a great amount of crazing or many small cracks.

40 Example 217

Following the procedure of the first paragraph of Example 216, except that the SiO layer was 31 nm thick and the SiO_2 layer contained 5% Cu (source composition) and was 273 nm thick, gave an oxygen transmission rate after retorting of 3.078 ml/m^2 Day Atm. For another sample of coated resin substrate, the thickness of the SiO layer was 51 nm and of the the SiO_2 /Cu layer was 250 nm and the oxygen transmission rate for this sample was 6.624 ml/m^2 Day Atm.

50 Example 218

In this Example, the resin substrate was a polyester film of poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) which had a rough surface characterized by visible ripples present in the film surface. A barrier film was formed by the vacuum deposition procedure of Example 210 with an SiO underlayer 50 nm thick on the PEN film and SiO_2 toplayer containing 5% Sn (source composition) and measuring 125 nm thick on the SiO underlayer. The OTR of the film prior to retorting was 1.8 ml/m^2 Day Atm and after retorting was 12.5 ml/m^2 Day Atm. The OTR of the PEN film by itself was 23 ml/m^2 Day Atm.

Example 219

A number of barrier films of the structure PET film/SiO/SiO₂ were formed by vacuum deposition by the procedure of Example 210, in which the PET film was Mylar D and the SiO₂ layer contained various dopants (source compositions reported based on the elemental metal of the dopant), and on which OTR values were obtained either before or after retorting in accordance with Example 211. The results are shown in Table X.

10

15

20

25

30

35

40

45

50

55

TABLE X

No.	<u>SiO₂ layer thickness, nm</u>	<u>SiO₂ layer thickness (nm), dopant (wt %)</u>	OTR before retort (ml/m ² Day Atm)	OTR after retort (ml/m ² Day Atm)
a.	32	270 10 Cr	0.93	-
b.	35	280 10 Cr	-	1.33
c.	30	217 10 Fe	7.49	-
d.	30	272 10 Fe	-	6.59
e.	57	254 5 In	0.42	-
f.	50	252 5 In	-	5.84
g.	30	273 5 Mn	-	3.27
h.	31	273 10 Mn	-	47.8
i.	51	250 5 PbO	-	4.37
j.	26	278 5 SnO ₂	1.07	-
k.	29	277 5 Zr	5.07	-
l.	26	279 20 Zr	0.74	-
m.	25	279 5 ZrO	0.50	-

For experiment k., the PbO was supplied in the form of a fused glass designated SF-6 available from Schott Glass Technologies, Inc. Duryea, PA, and contained a small proportion of SiO₂.

Comparison of experiments a. with b. and c. with d. show stabilizing effect of the dopants in the amounts used on oxygen permeability before and after retorting. The element In was less effective in the amount used, but the result after retorting was still more than 10 times better than the PET film by itself.

Mn as the dopant in experiment g. produced a barrier film with a useful oxygen impermeability after retorting, while the OTR value for experiment h. suggests that too much Mn was present in the SiO₂ layer.

Experiments j. through m. all gave barrier layers with useful oxygen impermeabilities.

10 Example 220

In this Example, The SiO underlayer was replaced by an SiO₂ layer to yield the following multilayer film structure: PET film/32 nm SiO₂/271 nm SiO₂ + 5% Cu (source compositions). The PET film was Mylar D. The vacuum deposition procedure of Example 210 was used and the retort procedure of Example 211 was used. The OTR of this structure after retorting was 92.5 ml/m² Day Atm. The structure was clear and transparent, giving no visual evidence that the oxygen barrier had failed. In addition, the SiO₂ layers were strongly adhered to the PET film as indicated by a peel strength of 144.5 g/cm exhibited by a nearly identical film structure.

20 Example 221

This Example shows the high transparency and low water vapor transmission of a number of multilayer structures of the present invention prepared by the procedure of Example 210 using the PET film of that Example as the resin substrate, details of these structures and light transmissions being reported in Table XI (light transmission) and Table XII (water vapor transmission).

Table XII
Visible Light Transmission

30	SiO Layer thickness(nm)	SiO ₂ Layer thickness(nm)	dopant(wt%)	% Light Transmission	
				400 nm	550 nm
	24	271	5 Cu	72.06	88.24
35	25	125	5 Sn	77.61	87.36
	50	252	5 Sn	77.33	78.28
	32	270	10 Cr	77.74	89.85
40	30	272	10 Fe	69.02	77.16
	57	254	5 In	75.60	88.47
45	30	273	5 Mn	73.66	80.17

These light transmissions compare favorably with the light transmission of the PET film used as the resin substrate, which by itself exhibited light transmissions of about 86% (400 nm) and almost 82% (550 nm) and especially favorably with the light transmissions of PET commodity packaging film, viz, about 69% (400 nm) and about 78% (550 nm). The transmission of the Sn, Fe, and Mn containing structures were measured after retorting by the procedure of Example 211.

Table XII
Water Vapor Transmission

	<u>SiO Layer</u> <u>thickness(nm)</u>	<u>SiO₂ Layer</u> <u>thickness(nm)</u>	<u>dopant(wt%)</u>	<u>Water Vapor</u> <u>Transmission</u> <u>(g/m² from 90%</u> <u>rel.hum. to</u> <u>50% rel.hum.)</u>
5				
10	32	272	5 Cu	0.93
	10	300	5 Cu	2.48
	27	277	5 Sn	1.40
15	31	273	5 Cu	1.24*
	36	281	5 Sn	1.24*
20	49	250	5 MgF	0.78*

* WVTR after retorting

In this Example, the metal dopant concentration is based on the source composition. Experience has shown that the relationship between the source composition and the SiO₂ layer composition is such that generally the proportion of dopant in the SiO₂ layer composition will be from about 40 to 150% greater than the proportion of dopant present in the source. From this relationship, the proportion of dopant in the SiO₂ layers formed in the foregoing Examples can be estimated.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended Claims.

Claims

1. A structure having superior barrier properties, comprising:
 - (a) a polymeric substrate, and
 - (b) a glassy coating of silicon dioxide doped with at least one metal selected from the group consisting of antimony, aluminum, chromium, cobalt, copper, indium, iron, lead, manganese, tin, titanium, tungsten, zinc, and zirconium, or lithium borate, said coating and metal dopant contained therein being present in an amount suitable to provide an oxygen transmission value through the coated structure of at most about 5 mL/day-m²-atm.
2. The structure of claim 1 wherein the amount of metal dopant is suitable to provide an oxygen permeation value for said glassy coating of at most about 3000 X 10⁻⁶ mL-mm/day-m²-atm.
3. The structure of claim 1 or 2 wherein the thickness of the glassy coating is about 20 to about 500 nm.
4. The structure of claim 1, 2 or 3 wherein the glassy coating of silicon dioxide is doped with a metal selected from the group consisting of copper, chromium, manganese, tin, and zinc.
5. The structure of claim 4 wherein the metal is copper.
6. The structure of claim 4 wherein the metal is tin.
7. The structure of any one of claims 1 to 6 wherein the amount of dopant metal is sufficiently low that the optical density of said glassy coating retains at least about 70% optical transmission at 550 nm.

8. The structure of any one of claims 1 to 7 wherein the amount of dopant metal calculated as elemental metal is about 0.5 to about 30 weight percent of the glassy coating.
9. The structure of any one of claims 1 to 8 wherein the polymeric substrate has a surface smoothness such that the average height of roughness is less than about 50 nanometers.
10. The structure of any one of claims 1 to 9 wherein the polymeric substrate is a film of polyester or polyamide.
11. The structure of claim 10 wherein the polyester is oriented polyethylene terephthalate.
12. The structure of any one of Claims 1 to 11 wherein a layer of SiO is present between said polymeric substrate and said coating of silicon dioxide.
13. A structure having superior barrier properties, comprising:
 - (a) a polymeric substrate, and
 - (b) a glassy coating of silicon dioxide doped with lithium borate in an amount suitable to provide an oxygen transmission value through the coated structure of at most about 5 mL/day-m²-atm.
14. A process for imparting barrier properties to a polymeric substrate, comprising the steps of:
 - (a) selecting a polymeric substrate; and
 - (b) vacuum depositing directly or indirectly onto said polymeric substrate a glassy coating derived from silicon dioxide and at least one metal selected from the group consisting of antimony, aluminum, chromium, cobalt, copper, indium, iron, lead, manganese, tin, titanium, tungsten, zinc, and zirconium; wherein the amount of said glassy coating and the amount of metal contained therein is suitable to provide an oxygen transmission value of at most about 5 mL/day-m²-atm.
15. A multilayer structure comprising a polymeric substrate of polyester or polyamide, a vacuum deposited layer of SiO of about 10 to 75 nm thickness on said substrate, and a vacuum deposited layer of SiO₂ of at least about 20 nm thickness on said SiO layer.
16. The multilayer structure of Claim 15 wherein said SiO layer has an atomic ratio of oxygen to silicon in said layer of from 0.6:1 to 1.4:1.
17. The multilayer structure of Claim 15 or 16 wherein said SiO₂ layer contains an effective amount of dopant to improve its barrier properties upon retorting of said multilayer structure.
18. The multilayer structure of Claim 17 wherein said dopant is a metallic material selected from the group consisting of Ti, Zr, Zn, Al, In, Pb, W, Cu, Sn, Cr, Fe, Mn, Sb, Co, Ba, and Mg, and mixtures thereof, and the amount thereof present in said SiO₂ layer is about 0.5 to 30% based on the total weight of the layer.
19. The multilayer structure of any one of Claims 15 to 18 having an oxygen transmission rate (OTR) of less than about 7 cc/m² Day Atm.
20. The multilayer structure of Claim 19 wherein said oxygen transmission rate is present both before and after retorting.
21. The multilayer structure of any one of Claims 15 to 20 in the form of a film.
22. The multilayer structure of any one of Claims 15 to 20 in the form of a container.
23. A process for forming a barrier structure from a resin substrate of polyester or polyamide polymer comprising vacuum depositing a layer of SiO of about 10 to 75 nm thickness on said container and vacuum depositing a layer of SiO₂ of at least about 20 nm thickness on said SiO layer, the resultant multilayer structure having an oxygen transmission rate (OTR) of less than about 7 cc/m² Day Atm.
24. The process of Claim 23 wherein metal dopant is vacuum deposited along with the vacuum deposition of said layer of SiO₂ so that said metal dopant is incorporated in said SiO₂ layer in effective amount to provide said OTR after retorting of said structure.

Figure 1

